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OPTICAL PROPERTIES OF ZnS: Mn NANOPARTICLES PREPARED BY CHEMICAL ROUTS

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Zinc sulfide doped with Mn is a well-studied material due to its luminescence characteristics among other interesting properties and, therefore, they have potential for their use in several optoelectronic devices. The present paper reports the synthesis and characterization of luminescent nanocrystals of ZnS doped with Mn and mercaptoethanol was used as the capping agent . Nanocrystals of zinc sulphide were prepared by chemical rout technique.The particle size of such nanocrystals was measured using XRD pattern and it is found to be in between 3nm - 5nm.The blue-shift in the absorption spectra was found with reducing size of the nanoparticles.It was also found that change in Mn concentrations does not make changes in the particle size but change in the molar concentration of the reactants changes the particle size. The photoluminescence emission peaks occurs at around 440 nm and 590 nm

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1. Introduction

Semiconductor nanocrystals have attracted growing interest during the last four decades [1,2]. This class of new materials has not only provided many unique opportunities but also exhibited novel optical and transport properties, which are potentially useful for technological applications [3] like indicators, analysis of water pollution, environmental studies, pathological investigations etc. Blue shift in the optical absorption spectrum, size dependent luminescence, enhance oscillator strength, non-linear optical effects, geometrical structure, chemical bonds, ionization potential, mechanical strength, melting point etc. are all affected by particle size. The change in the properties of nanoparticles is driven mainly by two factors, namely the increase in the surface to volume ratio and change in the electronic structure of the material due to quantum confinement effects.

ZnS is semiconducting materials, which has a wide band gap of 3.70eV [4, 5]. Zinc sulfide is well-studied material due to its luminescence characteristics among other interesting properties. With a good surface modification, one can obtain zinc sulfide nanoparticles, which have enhanced luminescence properties. In this work zinc sulfide nanocrystals are prepared by chemical precipitation technique and mercaptoethanol has been used for capping, which modifies surface of nanoparticles and prevents the growth of the particles to larger size. The effect of concentration of mercaptoethenol on the particle size, effect of changes in Mn concentrations on optical absorption

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spectra and the change in the molar concentration of the reactants on the particle size has been investigated.

2. Experimental

The most important step in the studies of nanoparticles is their synthesis. There are various methods supported for synthesis of nanoparticles. Chemical route is used in the present investigation. The powder of ZnS nanoparticles were prepared by using chemical deposition technique described by Khosravi [6]. For synthesis, the 1M aqueous solution of $ZnCl_2$ and 1M aqueous solution of Na_2S were mixed in the presence of various concentration of mercaptoethenol solution. $MnCl_2$ was also mixed in the solution in ratio 99:1, while stirring the solution continuously. The obtained precipitate was washed thoroughly three to four times in double distilled water and then separated by centrifuge at 3500 rpm, and finally air dried. Special care has to be taken to maintain the same physical condition during the synthesis of the sample.

All the samples were characterized at Inter University Consortium (IUC) Indore The morphologies and sizes of the mercaptoethanol capped ZnS:Mn were determined by X-ray diffraction studies with Cu Kα radiation (λ=1.5418 Å). XRD data were collected over the range 20^0-70^0 at room temperature.X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer . The particle size was calculated using the Debye-Scherrer formula.

Absorption spectra of the samples prepared with various concentrations of capping agent were studied. Perkin Elimer λ -12 spectrometer was used to obtain the absorption spectra of ZnS:Mn nanoparticles.

Photoluminescence of the samples prepared were studied by photomultiplier tube.

3. Results and discussion

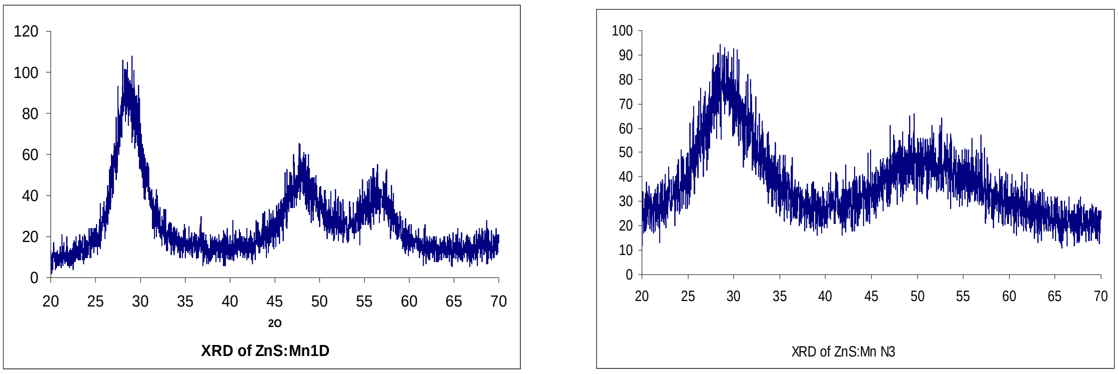

Fig. 1. XRD pattern of ZnS:Mn with molar concentration 1M and 10^{-2}M.

The XRD patterns for the samples are shown in Figure 1.Three different peaks are obtained at 2Θ values of 29.50 °, 48.80° and 57.80 °. This shows that the samples have zinc blende structure and the peaks correspond to diffraction at (111),(220) and (311) planes, respectively [7]. The lattice parameter has been computed as 5.31 Å, which is very close to the standard value (5.42 Å). The broad peak indicates nanocrystalline behavior of the particles. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [8]. It was also found that peaks get broadened for higher concentration of capping agent.

$$D = \frac{K\lambda}{\beta\cos\theta}$$

The XRD spectra of the ZnS:Mn nanoparticles with different molar concentration of the reactants are different . It is clear from the figure that the peak width is less for the samples with higher molar concentration (1M) to that of the lower molar concentration (10^{-2}M). The particle size of the sample for 1M concentration is 4.16 nm and 3.46 nm for 10^{-2}M is observed. The change in the particle size is due to the change in the rate of reaction.

The study of optical absorption is important to understand the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is the band gap-the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge. Figure (2a &2b) shows the optical absorption spectra of ZnS nanoparticles in the range of 400 nm-200 nm. It was found that the spectra are featureless and no absorption occur in visible region (800 nm-390 nm). Absorption edge was obtained at shorter wavelength. It was found that with the increasing concentration of mercaptoethanol the peak shifts towards the lesser value of wave length. The observed blue shift in the absorption edge is reflection of the band gap increase owing to quantum confinement effect. In the bulk material the band gap can be found from the graph between ($\alpha h\nu^2$) vs. hν whereas in the nanomaterials the band gap is obtained from the absorption maxima. The band gap energy of the samples corresponding to the absorption edge is found in the range 4.5eV- 4.8eV with increasing the capping agent concentration. Similar results are reported by Kumbhojkar *et al.*[9] and Ruby *et al.*[10].

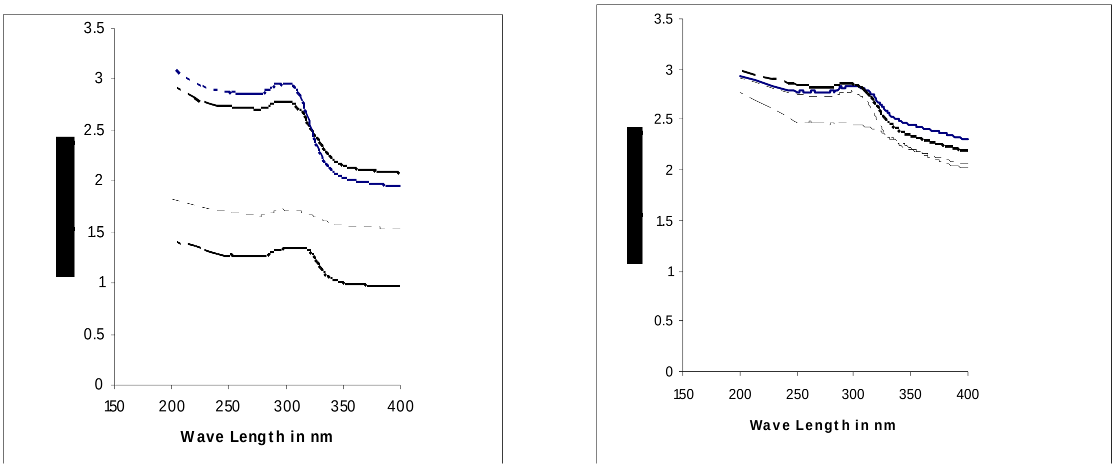

Fig. 2. (a)Optical absorption spectra with diff. concentration of mercaptothanol, (b) Optical Absorption spectra with diff. Mn%.

Fig. 2(b) shows the optical absorption spectra with different concentration of Mn where as the concentration of capping agent remains same. It was found that the peak position for all the samples is same with different intensity of absorption. Hence change in the concentration of Mn does not make any change in the absorption edge of the optical absorption spectra.

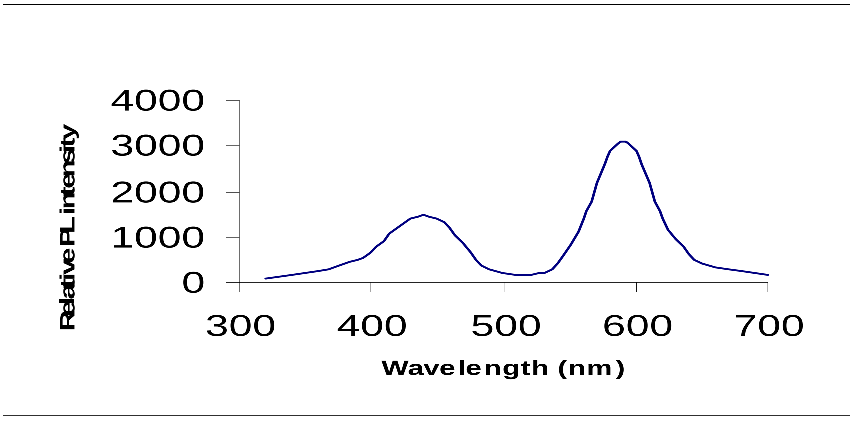

Fig. 3. The PL spectra of ZnS : Mn

Fig.3 shows the PL spectra of ZnS:Mn at room tempreture. The PL spectra was recorded by using gratting and photomultiplier tube, in which two peaks were obtained ; where the dominant peak occurs at 590 nm and the low intensity peak occurs at 440 nm. The peak at 590nm arises due to the excitation and subsequent de-excitation of mn^{2+} ions, and the peak at 440nm occurs because of the self- trapping hole centres in ZnS.

4. Conclusion

The nanoparticles of ZnS:Mn were grown by chemical routs in which mercaptoethanol was used as a capping agent . The size of nanoparticle was found to decrease with increasing concentration of mercaptoethanol. The change in the concentration of Mn does not change the particle size.The XRD pattern indicated the growth of the nanoparticles.The change in the molar concentration of reactants changes the particle size,at fixed concentration of the capping agent The measurement of optical absorption spectra indicated blue-shift with reducing size of the nanoparticles. Two peaks were obtained in the photoluminescence spectra of ZnS:Mn nanoparticles , where the dominant peak lies at 590nm and the low intensity peak lies at 440nm.

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